

Self-Assembly and X-ray Structure Determination of the Novel 2-D Layered Organic–Inorganic Hybrid Pb–X Compound: $[\text{PbX}_2(4,4'\text{-bipy})]_n$ ($\text{X} = \text{I}, \text{Br}$)

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Two novel organic–inorganic hybrid compounds, $[\text{PbI}_2(4,4'\text{-bipy})]_n$ (**1**) and $[\text{PbBr}_2(4,4'\text{-bipy})]_n$ (**2**), are synthesized by self-assembly. X-ray crystallography analysis shows that the $[\text{PbI}_2]_n$ chains in **1** are linked by 4,4'-bipyridine to form a layer, via Pb–N bonding along the direction of the 'b' axis.

Currently there is considerable interest in lead(II) halide compounds reflecting their potential applications due to their diverse electrical, magnetic and optical properties, as well as their excellent film processability.^{1–5} Lead(II) iodide compounds are of particular interest due to their significant third-order non-linear optical properties.^{6,7} Recently, an important advance in lead(II) halide chemistry has been achieved on the study of inorganic solid-state materials by incorporating organic moieties.^{8–22} Structures determined included $[\text{C}_6\text{H}_{10}\text{N}_2]_n\text{Pb}_2\text{I}_6\cdot 3\text{thf}$ ¹⁰ and $[\text{H}_3\text{N}(\text{CH}_2)_6\text{NH}_3]\text{PbI}_4$,¹⁵ with two-dimensional layered structure, $[\text{CH}_3\text{SC}(=\text{NH}_2)\text{NH}_2]_3\text{PbI}_5$ ¹⁶ and $\text{PbI}_2(\text{L})$ ($\text{L} = 2,2'$ -bipyridine, 1,10-phenanthroline),¹⁷ with one-dimensional infinite extended structure, and the compound $(\text{Bu}_4\text{N})_8[\text{Pb}_{18}\text{I}_{44}]$,¹⁸ having discrete $[\text{Pb}_{18}\text{I}_{44}]^{8-}$ anion. Czakis Sulikowska and co-workers²³ have reported the synthesis, properties and infrared spectra of lead(II) complexes with 2,2'-bipyridine and 4,4'-bipyridine, however, to our knowledge, X-ray crystal structure of $[\text{PbI}_2(4,4'\text{-bipy})]_n$ (**1**) has not been reported. We report herein the synthesis of two lead(II) compounds, **1** and $[\text{PbBr}_2(4,4'\text{-bipy})]_n$ (**2**), and the structural determination of **1**.

The compound **1**²⁴ was prepared by reacting 4,4'-bipyridine with PbI_2 in solution. Slow addition of a methanol solution of 4,4'-bipyridine (0.078 g, 0.5 mmol) to a dimethylformamide (DMF) solution of PbI_2 (0.230 g, 0.5 mmol) gave a yellow precipitate, which was filtered and washed with methanol. The compound **2**²⁴ was prepared by the method similar to that for compound **1**. Single crystals of **1** were grown at room temperature using a layered solution approach. The bottom solution layer, contained within a long straight tube, consists of PbI_2 dissolved in DMF. A mixed-solvent layer of methanol/DMF was carefully placed on top of the PbI_2 solution using a syringe. Finally, 4,4'-bipyridine (a stoichiometric quantity relative to the PbI_2) dissolved in methanol was added to the top of the buffer. As the layers slowly diffuse together, well-formed crystals of (**1**) appear, suitable for X-ray single-crystal analysis.

The single-crystal X-ray analysis of the orange plates revealed compound **1**²⁵ as a layered structure containing organic–inorganic hybrid layers $[\text{PbI}_2(4,4'\text{-bipy})]_n$, running parallel to the (1 0 0) plane, as shown in Figure 1. The $[\text{PbI}_2(4,4'\text{-bipy})]_n$ layers are separated from each other by a distance of 6.46 Å along the 'a' axis. They form very weak hydrogen bonds with the adjacent Pb–I–L ($\text{L} = \text{ligand}$) layers. The iodine atoms'

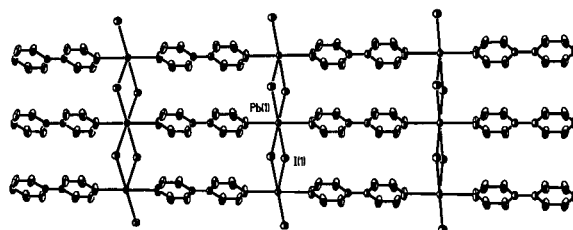


Figure 1. A plot of the structure showing the unit-cell packing as viewed into the *c* axis.

closest contacts with the carbon atoms of 4,4'-bipyridyl are between $\text{I}_1 \cdots \text{C}_{1a}$ ($-x, 1-y, -z-1$) at 3.99(2) Å, and the $\text{I}_1 \cdots \text{C}_{2a}$ ($x-0.5, 0.5+y, 1+z$) at 4.02(2) Å, respectively. As shown in Figure 2, the unusual feature of compound (**1**) is that the organic–inorganic hybrid layer is constructed from the $[\text{PbI}_2]_n$ chains linked by 4,4'-bipyridine. The infinite chains of edge-sharing distorted PbI_4N_2 octahedron are running parallel to the 'c' axis, and linked by 4,4'-bipyridine using Pb–N bond along the direction of the 'b' axis, giving a layer composition of $[\text{PbI}_2(4,4'\text{-bipy})]_n$.

There is only one type of iodine atoms coordinated to two lead atoms. Also, only one type of lead atoms were observed in the $[\text{PbI}_2]_n$ chains, and each lead atom is bonded by four doubly bridged iodine atoms and two nitrogen atoms of 4,4'-bipyridine, with the bond distances of Pb–I(2b), 3.1911(12)–3.2053(11) Å

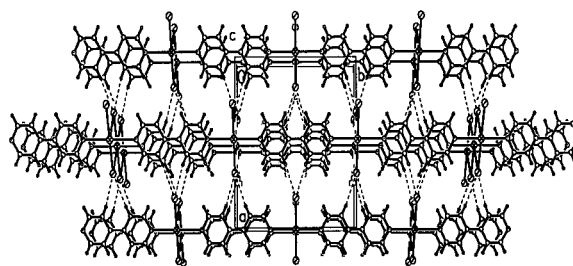


Figure 2. ORTEP representation of the structure of $[\text{PbI}_2]_n$ chains bonded by 4,4'-bipyridine looking down the 'a' axis. Important distances (Å) and angles (°) are: Pb(1)–N(1) 2.658(10), Pb(1)–I(1)ⁱⁱ 3.1911(12), Pb(1)–I(1) 3.2053(11), N(1)–C(1) 1.321(14), C(1)–C(2) 1.390(15), C(2)–C(3) 1.382(12), N(1)ⁱ–Pb(1)–N(1) 180.0, N(1)ⁱ–Pb(1)–I(1)ⁱⁱ 90.0, N(1)–Pb(1)–I(1)ⁱⁱⁱ 90.0, I(1)ⁱⁱ–Pb(1)–I(1)ⁱⁱⁱ 180.0, N(1)–Pb(1)–I(1) 90.0, I(1)ⁱⁱ–Pb(1)–I(1) 87.94(2), I(1)ⁱⁱⁱ–Pb(1)–I(1) 92.06(2), I(1)ⁱⁱ–Pb(1)–I(1)ⁱ 92.06(2), I(1)–Pb(1)–I(1)ⁱ 180.0, Pb(1)^{iv}–I(1)–Pb(1) 87.94(2), C(1)^v–N(1)–C(1) 116.0(11), C(1)–N(1)–Pb(1) 122.0(6), N(1)–C(1)–C(2) 124.1(10), C(3)–C(2)–C(1) 119.8(10). i: $-x, -y+1, -z-1$, ii: $x, y, z-1$, iii: $-x, -y+1, -z$, iv: $x, y, z+1$, v: $-x, y, -z-1$.

and Pb–N, 2.658(10) Å, respectively. These bond lengths for Pb–I and Pb–N can be compared with the other lead complexes.¹

In one hybrid layer, the shortest distance between lead atoms is 4.44(1) Å for Pb(1)⋯Pb(1a) (x, 1+y, z). In contrast to those related structures reported in literatures, however, in **1**, very weak intermolecular π – π stacking interactions between the C₁-pyridyl ring and its symmetry partner at (x, 1+y, z) are observed along the 'c' axis, with a perpendicular distance of 4.41(1) Å. To our knowledge, although the two-dimensional layered lead halide hybrid has been reported in literature,^{10,15} the case that inorganic (PbI₂)_n chains bonded by organic ligand to form a two-dimensional organic–inorganic hybrid layered structure has not been discovered in the other complexes in Pb–I system, indicating the present compound is a new system.

Czakis Sulikowska and co-workers reported that lead(II) complexes with 2,2'-bipyridine and 4,4'-bipyridine reveal luminescence in UV light at room temperature.²³ We investigate the emission spectrum for (**1**) at room temperature, which shows a peak at 530 nm, when the solid state sample was excited at 400 nm, as shown in Figure 3. There is a 38 nm blue shift as compared with the emission spectrum for PbI₂(2,2'-bipyridine),¹⁷ which may arise from the difference of coordination modes between 4,4'-bipyridine and 2,2'-bipyridine. The emission peak position for (**1**) was independent of the excitation wavelength, similar to that of the (C₄H₉NH₃)₂PbI₄ thin film.¹⁹ Further studies are in progress in our laboratory.

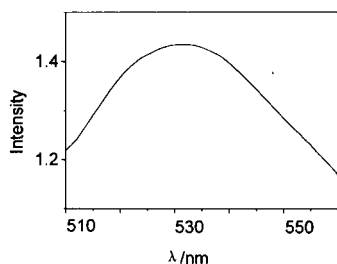


Figure 3. Emission spectrum of (**1**) excited at 400 nm for the solid sample at room temperature.

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References and Notes

- 1 D.B. Mitzi, *Prog. Inorg. Chem.*, **48**, 1 (1999).
- 2 D.B. Mitzi, S. Wang, C.A. Field, W.T.A. Harrison, and A.M. Guloy, *Nature*, **369**, 467 (1994).
- 3 T. Ishihara, J. Takahaashi, and T. Goto, *Phys. Rev. B*, **42**, 11099 (1990).
- 4 D.B. Mitzi, S. Wang, C.A. Field, C.A. Chess, and A.M. Guloy, *Science*, **267**, 1473 (1995).
- 5 D.B. Mitzi, C.A. Field, Z. Schlesinger, and R.B. Laibowitz, *J. Solid State Chem.*, **114**, 159 (1995).
- 6 J. Calabrese, N.L. Jones, R.L. Harlow, N. Herron, D.L. Thorn, and Y. Wang, *J. Am. Chem. Soc.*, **113**, 2328 (1991).
- 7 G.C. Papavassiliou, A.P. Patsis, D.J. Lagouvardos, and I.B. Koutselas, *Synth. Met.*, **55–57**, 3887 (1993).
- 8 X. Hong, T. Ishihara, and A.V. Nurmikko, *Phys. Rev. B*, **45**, 6961 (1992).
- 9 G.C. Papavassiliou and I.B. Koutselas, *Synth. Met.*, **71**, 1713 (1995).
- 10 V. Chakravarthy and A.M. Guloy, *Chem. Commun.*, **1997**, 697.
- 11 N. Kitazawa, *Jpn. J. Appl. Phys.*, **35**, 6202 (1996).
- 12 N. Kitazawa, *Jpn. J. Appl. Phys.*, **36**, 2272 (1997).
- 13 M. Era, S. Morimoto, T. Tsutsui, and S. Saito, *Appl. Phys. Lett.*, **65**, 676 (1994).
- 14 T. Fujita, Y. Sato, T. Kuitani, and T. Ishihara, *Phys. Rev. B*, **57**, 12428 (1998).
- 15 G.A. Mousdis, G.C. Papavassiliou, C.P. Raptopoulou, and A. Terzis, *J. Mater. Chem.*, **10**, 515 (2000).
- 16 G.A. Mousdis, V. Gionis, G.C. Papavassiliou, C.P. Raptopoulou, and A. Terzis, *J. Mater. Chem.*, **8**, 2259 (1998).
- 17 H.G. Zhu, Y. Xu, Z. Yu, Q.J. Wu, H.K. Fun, and X.Z. You, *Polyhedron*, **18**, 3491 (1999).
- 18 H. Krautscheid and F. Vielsack, *Angew. Chem., Int. Ed. Engl.*, **34**, 2035 (1995).
- 19 D.B. Mitzi, M.T. Prikas, and K. Chondrodiss, *Chem. Mater.*, **11**, 542 (1999).
- 20 K. Liang, D.B. Mitzi, and M.T. Prikas, *Chem. Mater.*, **10**, 403 (1998).
- 21 G.C. Papavassiliou, G.A. Mousdis, C.P. Raptopoulou and A. Terzis, *Z. Naturforsch., B*, **54**, 1405 (1999).
- 22 S. Wang, D.B. Mitzi, C.A. Field, and A. Guloy, *J. Am. Chem. Soc.*, **117**, 5297 (1995).
- 23 D.M. Czakis-Sulikowska, J. Radwanska-Doczekalska, and A. Gorecka, *Rocz. Chem.*, **47**, 2435 (1973).
- 24 Calcd for [PbI₂(4,4'-bipy)]_n: C, 19.42; H, 1.29; N, 4.53%. Found: C, 19.86; H, 1.41; N, 4.40%. and Calcd. for [PbBr₂(4,4'-bipy)]_n: C, 22.96; H, 1.54; N, 5.35%. Found: C, 22.72; H, 1.67; N, 5.17%.
- 25 The crystal data for **1**: $F_w = 617.17$, diffraction data were collected on a crystal with dimensions 0.20×0.16×0.14 mm³ using a CAD 4 diffractometer and Mo K α radiation at 293 K, monoclinic, space group C2/m, $a = 12.924(3)$, $b = 12.413(3)$, $c = 4.4410(9)$ Å; $\beta = 95.64(3)^\circ$; $Z = 2$, $F(000) = 540$, $D_c = 2.891$ g/cm³. Of 1433 data collected ($\theta_{\max} = 25^\circ$), 664 were independent ($R_{\text{int}} = 2.86\%$) and 609 were observed. An empirical absorption correction from ψ -scans was applied ($\mu = 16.226$ mm⁻¹). All non-hydrogen atoms were refined anisotropically. $R_1 = 0.0246$, $wR_2 = 0.0737$.